THE VISCOSITY OF VAPOURS OF ORGANIC COMPOUNDS. PART II.

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Experiments on the transpiration method have been continued for various organic gases, using the capillary viscosimeter recently devised by the writer.(1) As described in the preceding paper air has been taken as standard substance, its viscosity being assumed to be equal to Millikan's value 1823×10^{-7} at 23°C.; and the values for other substances have been determined by relative measurement. Present work includes the measurements for seventeen gases at temperatures ranging between 20° and 120°C. and the computation of Sutherland's constants and molecular diameters for each of them. The gases used and their preparations are as follows:

Ethane: obtained by the electrolysis of potassium acetate, thoroughly washed with potassium hydroxide solution, condensed and then repeatedly fractionated.

Propane and isobutane: obtained by the action of Zn–Cu couple on dilute alcoholic solution of isopropyl- or isobutyl-iodide, condensed and fractionated.

Normal butane: prepared by the action ef sodium amalgam on ethyl-iodide and purified by fractional distillation.

Ethylene and propylene: obtained by dehydrating ethyl- or iso-propyl-alcohol with hot concentrated phosphoric acid.

α- and β-butylene: obtained by the action of alcoholic potash on n-butyl- or secondary butyl-iodide and puried by fractional distillation.

γ-butylene: obtained by dehydrating tertiary butyl alcohol with hot anhydrous oxalic acid and purified by fractional distillation.

Isoamylene (isopropyl-ethylene): obtained by the action of alcoholic potash on isoamyl-iodide prepared from Kahlbaum's isoamyl alcohol, shaken with two volumes dilute sulphuric acid at 0°C. for two hours(2) and then fractionated.

(1) This Bulletin, **4** (1929), 277.
(2) Wischnegradsky, *Ann.*, **190** (1878), 353.

Acetylene: prepared from calcium carbide and water and purified after Vanino.(1)

Allylene: obtained by the action of alcoholic potash on propylene-bromide, precipitated as copper compound, regenerated by warm dilute hydrochloric acid and fractionated.

Trimethylene: prepared by the reduction of trimethylene-bromide with zinc dust and alcohol, washed with potassium permanganate solution and fractionated.

Methyl-ether: obtained by dehydrating methyl alcohol with hot concentrated phosphoric acid, alcohol vapour mixed having been absorbed with phosphorus pentoxide.

Methyl-chloride: obtained by the action of dry hydrogen chloride gas on the boiling mixture of methyl alcohol and zinc chloride, washed with dilute potassium hydroxide solution and fractionated.

Methyl-bromide: obtained by heating the mixture of methyl alcohol, potassium bromide and dilute sulphuric acid, washed with water and fractionated.

Sulphur-dioxide: taken from a steel bomb and dried with sulphuric acid.

The gases hardly soluble in water were all thoroughly washed with water and dried with calcium chloride before distillation.

The results of measurements are shown in the following tables. Sutherland's formula has been found to be applicable with satisfactory results for all gases. The viscosity values calculated by this formula are given in the third column. For the sake of comparison other observers' values are also cited, of which the figures with asterisk have been estimated graphically from original observed values.

Ethane.

$$\eta=107.15\frac{T^{3/2}}{T+287.3}\cdot 10^{-7}$$

t°C.	$\eta\cdot 10^7$		Other observers' values
	Obs.	Calc.	
0	—	863	855 (Vogel(2) 1914)
20	929	926	917*(Ishida(3) 1923)
40	986	989	—
60	1050	1050	—
80	1111	1110	—
100	1167	1169	—
120	1230	1227	—

(1) Vanino, "Handbuch d. präparativen Chemie," II, 2. Aufl., (1923).
(2) Vogel, *Ann. Phys.*, **43** (1914), 1235.
(3) Ishida, *Phys. Rev.*, **21** (1923), 550.

Propane.

$$\eta=102.3\frac{T^{3/2}}{T+341.3}\cdot 10^{-7}$$

t°C.	$\eta\cdot 10^7$		Other observers' value
	Obs.	Calc.	
0	—	751	752 (Klemenc & Remi,(1) 1923)
20	806	809	—
40	873	866	—
60	922	922	—
80	978	977	—
100	1029	1032	—
120	1082	1085	—

Normal butane.

$$\eta=98.27\frac{T^{3/2}}{T+377.4}\cdot 10^{-7}$$

t°C.	$\eta\cdot 10^7$		Other observers' values
	Obs.	Calc.	
0	—	682	852*(Kuenen and Visser,(2) 1913)
20	739	735	—
40	787	789	—
60	839	841	—
80	885	893	—
100	947	944	1092 (,,)
120	998	994	—

Isobutane.

$$\eta=92.85\frac{T^{3/2}}{T+335.5}\cdot 10^{-7}$$

t°C.	$\eta\cdot 10^7$		Others observer's value
	Obs.	Calc.	
0	—	689	—
20	744	741	747*(Ishida(3) 1923)
40	792	793	—
60	845	844	—
80	888	895	—
100	947	944	—
120	995	993	—

(1) Klemenc and Remi, *Monatsh. Chem.*, **44** (1923), 307.

(2) Kuenen and Visser, *Verhandel. Akad. Wetenschappen Amsterdam*, **22** (1913), 336; *Comm. Phys. Lab. Univ. Leiden*, No. 138 a.

(3) Ishida, loc. cit.

Ethylene.

$$\eta=107.0\frac{T^{3/2}}{T+259.1}\cdot 10^{-7}$$

t°C.	$\eta \cdot 10^7$		Other observers' values
	Obs.	Calc.	
0	—	907	966 (Graham,[1] 1846) 922 (v. Obermayer,[2] 1875) 961 (Breitenbach,[3] 1901) 907 (Zimmer,[4] 1911)
20	—	972	1090 (Graham) 987*(v. Obermayer) 1032*(Breitenbach) 974*(Zimmer)
22	970	979	—
40	1036	1036	—
60	1109, 1106 } 1108	1098	1116*(v. Obermayer)
80	1155, 1153 } 1154	1160	—
100	1223, 1217 } 1220	1220	1280*(Breitenbach)
120	1278, 1280 } 1279	1279	—

Propylene.

$$\eta=103.2\frac{T^{3/2}}{T+321{\cdot}6}\cdot 10^{-7}$$

t°C.	$\eta \cdot 10^7$	
	Obs.	Calc.
0	—	783
20	835	842
21.5	856	847
40	893	901
60	959	958
80	1023	1015
100	1071	1070
120	1122	1125

(1) Graham, *Phil. Trans.*, **3** (1846), 573.
(2) v. Obermayer, *Wien. Ber.*, **71** [2a], (1875), 281.
(3) Breitenbach, *Ann. Phys.*, **5** (1901), 166.
(4) Zimmer, Diss. Halle, (1911); *Verhandl. deut. physik. Ges.*, **14** (1912), 471.

α—butylene.

$$\eta = 94.48 \frac{T^{3/2}}{T + 328.9} \cdot 10^{-7}$$

t°C.	$\eta \cdot 10^7$	
	Obs.	Calc.
0	—	708
20	761	762
40	819	815
60	863	868
80	922	919
100	971	970
120	1020	1020

β—butylene.

$$\eta = 97.63 \frac{T^{3/2}}{T + 362.1} \cdot 10^{-7}$$

t°C.	$\eta \cdot 10^7$	
	Obs.	Calc.
0	—	694
25	761	761
40	796	801
60	858	854
80	905	906
100	961	957
120	1005	1008

γ—butylene.

$$\eta = 99.21 \frac{T^{3/2}}{T + 339.0} \cdot 10^{-7}$$

t°C.	$\eta \cdot 10^7$	
	Obs.	Calc.
0	—	732
30	815	815
40	843	843
60	897	897
80	949	951
100	1006	1004
120	1056	1056

Isoamylene (Isopropyl-ethylene).

$$\eta=94.48\frac{T^{3/2}}{T+368.0}\cdot 10^{-7}$$

$t°$ C.	$\eta\cdot 10^7$	
	Obs.	Calc.
0	—	665
22	714	722
40	771	769
50	793	794
60	829	819
80	871	869
100	915	919
120	967	968

Acetylene.

$$\eta=99.59\frac{T^{3/2}}{T+198.2}\cdot 10^{-7}$$

$t°$ C.	$\eta\cdot 10^7$		Other observer's value
	Obs.	Calc.	
0	—	954	943 (Vogel,[1] 1914)
20	1020	1017	—
40	1079	1079	—
50	1113	1110	—
60	1131	1140	—
80	1198	1199	—
100	1254	1256	—
120	1318	1313	—

Allylene.

$$\eta=98.35\frac{T^{3/2}}{T+276.5}\cdot 10^{-7}$$

$t°$ C.	$\eta\cdot 10^7$	
	Obs.	Calc.
0	—	808
10	—	837
20	867	866
30	895	895
40	925	924
50	952	953
60	977	981
70	1009	1009
80	1039	1036
90	1066	1064
100	1090	1091

(1) Vogel, loc. cit.

Trimethylene.

$$\eta=115.3\frac{T^{3/2}}{T+372.0}\cdot 10^{-7}$$

t°C.	$\eta\cdot 10^7$ Obs.	$\eta\cdot 10^7$ Calc.
0	—	807
20	876	870
40	923	933
50	960	964
60	999	994
80	1057	1055
100	1113	1115
120	1179	1175

Methyl-ether.

$$\eta=116.4\frac{T^{3/2}}{T+344.9}\cdot 10^{-7}$$

t°C.	$\eta\cdot 10^7$ Obs.	$\eta\cdot 10^7$ Calc.	Other observers' values
0	—	850	905 (Graham,(1) 1846)
19.5	909	914	—
20	—	915	1020 (,,)
40	984	980	—
60	1044	1043	—
80	1109	1106	—
100	1167	1168	1190 (Pedersen,(2) 1907)
120	1228	1229	—

Methyl-chloride.

$$\eta=142.3\frac{T^{3/2}}{T+380.1}\cdot 10^{-7}$$

t°C.	$\eta\cdot 10^7$ Obs.	$\eta\cdot 10^7$ Calc.	Other observers' values(3)
0	—	983	1025 (Graham, 1846) 989 (Breitenbach, 1901) 978 (Vogel, 1914)
10	—	1022	—
20	1061	1061	1160 (Graham) 1072*(Breitenbach)
30	1101	1099	—
40	1140	1137	—
50	1175	1175	—
60	1209	1213	—
70	1250	1251	—
80	1287	1288	—
90	1323	1325	—
100	1357	1362	1388*(Breitenbach)
110	1400	1398	—
120	1440	1434	—
130	1471	1470	—

(1) Graham, loc. cit. (2) Pedersen, *Phys. Rev.*, **25** (1907), 225. (3) Loc. cit.

Methyl-bromide.

$$\eta = 177.5 \frac{T^{3/2}}{T+379.2} \cdot 10^{-7}$$

t° C.	$\eta \cdot 10^7$ Obs.	$\eta \cdot 10^7$ Calc.
0	—	1228
10	1277	1277
20	1327	1325
21	1333	1330
30	1378	1373
40	1420, 1412 } 1416	1421
50	1457	1468
60	1512, 1522 } 1517	1515
120	1797	1791

Sulphur-dioxide.

$$\eta = 173.6 \frac{T^{3/2}}{T+395.8} \cdot 10^{-7}$$

t° C.	$\eta \cdot 10^7$ Obs.	$\eta \cdot 10^7$ Calc.	Other observers' values.
0	—	1171	1225 Graham,(1) 1846) 1183 (Vogel,(2) 1914) 1168 (Smith,(3) 1922)
20	1266	1265	1380 (Graham) 1263* (Smith) 1250* (Trautz and Weizel,(4) 1925)
40	1352	1357	1345* (,,)
60	1455	1448	—
80	1540	1538	1533* (Trautz and Weizel)
100	1622	1627	1630 (Smith) 1625* (Trautz and Weizel)
120	1716	1715	1720* (,,)

(1) Graham, loc. cit.
(2) Vogel, loc. cit.
(3) Smith, *Phil. Mag.*, [vi], **44** (1922), 508.
(4) Trautz and Weizel, *Ann. Phys.*, [4], **78** (1925), 305.

Sutherland's constants C for various gases are said to be proportional to the critical point T_K or the boiling point T_S expressed in absolute scale, being equal to $\frac{T_K}{1.12}$ according to Rankine[1] or to $1.47T_S$ according to Vogel.[2] The above results show that the relations do not hold strictly and the discrepancy from the rules is often remarkable, as is seen from the next table.

Sutherland's Constants.

Substance	$C_{obs.}$	$\frac{T_K}{1.12}$	$1.47\,T_S$	Other observers' values[3]
Ethane	287	275	272	—
Propane	341	330	335	323.7 (Klemenc and Remi)
Normal butane	377	380	400	349 (Kuenen and Visser)
Isobutane	336	363	387	—
Ethylene	259	253	249	272 (Sutherland) 226 (Breitenbach) 272 (O. E. Meyer and Zimmer)
Propylene	322	326	332	
α-butylene	329	372	393	
β-butylene	362	382	403	
γ-butylene	339	372	391	
Isoamylene	368	—	432	
Acetylene	198	276	278	
Allylene	277	360	366	
Trimethylene	372	—	350	
Methyl-ether	345	360	368	
Methyl-chloride	380	371	366	454 (Breitenbach)
Methyl-bromide	379	417	409	
Sulphur-dioxide	396	384	386	416 (Smith)
Air	113	118	119	Cf. the Part I of this paper

Mean free pathes (l) and collision diameters (σ) of molecules were calculated by the kinetic theory of gases using the following equations, where $\bar{u}$ expresses mean velocity, M molecular weight and n the number of molecules in one cubic centimeter, all referred to 0°C. and one atmospheric pressure.

(1) Rankine, *Proc. Roy. Soc. London*, [A], **84** (1910), 181.
(2) Vogel, loc. cit.
(3) Landolt-Börnstein-Roth, "Physikalisch-chemische Tabellen," I, 5. Aufl., (1923).

$$\bar{u}^2 = \frac{8}{\pi}\frac{p}{d} = \frac{8}{\pi} \times 1\,013\,250 \times \frac{22\,412}{M}$$

$$l = \frac{32\eta}{5\pi d\bar{u}} = \frac{\eta \times 22\,412}{0.49 \times M \times \bar{u}}$$

$$\sigma^2 = \frac{1}{\sqrt{2}\, n \pi l \left(1 + \frac{C}{T}\right)} \cdot \qquad (n = 2.7 \times 10^{19})$$

The next table contains the results of calculation :

Substance	M	$\bar{u}$	$\eta \cdot 10^7$	$l \cdot 10^8$	C	$\sigma \cdot 10^8$
Ethane	30.05	43 870	863	299	287	3.68
Propane	44.06	36 230	751	215	341	4.15
Normal butane	58.08	31 550	682	170	377	4.53
Isobutane	58.08	31 550	689	172	336	4.66
Ethylene	28.03	45 420	907	326	259	3.62
Propylene	42.05	37 090	783	230	322	4.08
α-butylene	56.06	32 120	708	180	329	4.58
β-butylene	56.06	32 120	694	176	362	4.51
γ-butylene	56.06	32 120	732	186	339	4.47
Isoamylene	70.08	28 730	665	151	368	4.84
Acetylene	26.02	47 150	954	356	198	3.68
Allylene	40.03	38 010	808	243	277	4.13
Trimethylene	42.05	37 090	807	237	372	3.86
Methyl-ether	46.05	35 440	850	238	345	3.93
Methyl-chloride	50.48	33 850	983	263	380	3.64
Methyl-bromide	94.94	24 680	1 228	240	379	3.81
Sulphur-dioxide	64.06	30 040	1 171	278	396	3.49
Air	28.99	44 660	1 711	604	113	3.12

The molecular diameters (σ_η) thus calculated from viscosity agree generally with those (σ_b) from van der Waals' b, deduced from critical data[1] as is seen in the following table.

(1) Valentiner, Landolt-Börnstein-Roth, "Physikalisch-chemische Tabellen," I, 5. Aufl., (1923), 253; Pickerring, *J. Phys. Chem.*, **28** (1924), 97.

Molecular diameters.

Substance	$\sigma_\eta \cdot 10^8$	$\sigma_b \cdot 18^8$	$\sqrt[3]{V_S}$
Ethane	3.68	3.70	3.84
Propane	4.15	4.05	4.21
Normal butane	4.53	4.59	4.58
Isobutane	4.66	4.48	4.57
Ethylene	3.62	3.56	3.54
Propylene	4.08	4.02	4.05
α-butylene	4.58	—	4.46
β-butylene	4.51	—	4.46
γ-butylene	4.47	—	4.45
Isoamylene	4.84	4.80	4.79
Acetylene	3.68	3.44	3.33
Allylene	4.13	—	3.90
Trimethylene	3.86	—	3.92
Methyl-ether	3.93	3.85	3.97
Methyl-chloride	3.64	3.71	3.69
Methyl-bromide	3.81	-	3.82
Sulphur-dioxide	3.49	3.55	3.53
Air	3.12	3.06	3.11

The figures in the last column express the cube root of the molecular volumes at boiling points. These values shall be proportional to the actual diameters of molecules according to the theory of corresponding state and it seems to be actually the case. Indeed, if 10^{-8} be affixed to the figures in the last column, they express the actual dimensions of molecules. This result shows the molecular volumes at boiling points being about three times as large as the actual volume of molecules:

$$6.06 \times 10^{23} \cdot \frac{\pi}{6} \sigma^3 \doteqdot 0.318 V_s .$$

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